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(71) Applicant (<i>for all designated States except US</i>): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).		Published <i>With international search report.</i>	

(54) Title: LOW COEFFICIENT OF FRICTION SURFACE

(57) Abstract

Solid shaped structure having a surface coated with crosslinked hydrophilic polymer, and process for preparing such structure, the coating being durable and exhibiting a low coefficient of friction when wet.

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TITLE

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Low Coefficient Of Friction Surface

BACKGROUND OF THE INVENTIONField of the Invention

10 This invention relates to shaped structures having low friction surfaces when wet.

Background

15 U.S. 4,585,666 discloses a process for coating a polymer surface with a hydrophilic coating having low friction in wet condition. The process consists of applying to the polymer surface a solution containing between 0.05 to 40% of a compound which contains at least two unreacted 20 isocyanate groups per molecule, evaporating the solvent, applying a solution containing between 0.5 to 50% of polyvinylpyrrolidone to the thus treated polymer surface, evaporating the solvent, and curing the coating at elevated temperature.

25 U.S. 4,503,111 discloses a recording material, comprising a hydrophobic substrate material with a polymeric coating. In a typical example a Mylar™ film is coated with a 5% solution of 360,000 MW polyvinylpyrrolidone dissolved in a 50:50 (by volume) mixture of ethanol/water. The product was air dried and tested on an ink jet 30 printer.

U.S. 4,119,094 and U.S. 4,100,309 disclose a substrate coated with a polyvinylpyrrolidone polyurethane interpolymer. In the method, a polyisocyanate and a polyurethane in a solvent such

as methyl ethyl ketone are applied to a substrate and the solvent is evaporated. If the substrate is a polyurethane, only the polyisocyanate need be employed. Polyvinylpyrrolidone in a solvent is then applied to the treated substrate and the solvent is evaporated.

The substrate can be, for example, a tube such as a catheter, a condom or a peristaltic pump tube.

U.S. 4,055,682 discloses a process whereby a silicone catheter is rendered hydrophilic by contacting it with N-vinyl pyrrolidone (NVP) in bulk or in solution and exposing the catheter and NVP to ionizing radiation at high dose rate. Penetration of the NVP beyond a thin surface layer is prevented by controlling the dosage of ionizing radiation and the concentration of NVP.

U.S. 3,892,575 discloses a method of modifying the surface properties of substrates such as films of plastics material. The substrate is given a very thin coating of a mixture of modifying materials and the latter is then bonded to the substrate by irradiation with ultra-violet light.

In a typical example a 1% solution of polyvinylpyrrolidone with added saponin is coated in a thin layer on a sheet of poly(ethylene terephthalate). The wet sheet is heated to about 100°C and irradiated for 1 minute with a germicidal ultraviolet lamp. The resulting hydrophilic coating resists moderate abrasion and cannot be removed by adhesive tape.

U.S. 4,589,873 discloses a method of coating a polymeric substrate, the method comprising contacting a polymeric substrate with a solution of polyvinylpyrrolidone in an applying solvent

selected from dimethyl formamide, butanone, methanol, tetrahydrofuran and dimethyl acetamide, and evaporating the solvent from the substrate so that the surface of the substrate retains a coating of the polyvinylpyrrolidone, to provide the surface of the coated substrate with lubricity when it is contacted with an aqueous-based liquid.

None of the above references either teaches or suggests the use of crosslinked hydrophilic polymers for the preparation of a solid shaped structure with a durable surface having a low coefficient of friction in wet condition.

RELATED CASE

This application is a continuation-in-part of my copending application U.S. Serial No. 07/172,183.

SUMMARY OF THE INVENTION

The invention resides in a solid shaped structure, such as a tubing, film, containment vessel or fiber, having at least one surface coated with a crosslinked hydrophilic polymer, the coated surface of the shaped structure being durable and having a low coefficient of friction in wet condition for extended periods of time.

By "wet" is meant that the substrate is in contact with a liquid, such as but not limited to, water; low molecular weight alcohols, such as methanol and ethanol; salt solutions; blood; and body fluids.

The invention also resides in a process which provides a solid surface which is durably coated with a crosslinked hydrophilic polymer, the process comprising contacting the solid surface with a

solution containing at least 0.1 wt. % of uncrosslinked hydrophilic polymer and a free radical initiator selected from peroxides and ultraviolet (UV) light-activated free radical initiators, air drying the coated solid surface, and heating the dried coated surface at the decomposition temperature of the free radical initiator or, when a UV light-activated free radical initiator is used, exposing the coated surface to UV radiation.

Alternatively, the process can be carried out by contacting the solid surface with a solution containing at least 0.1 wt. % of uncrosslinked hydrophilic polymer, air drying the coated solid surface, and subjecting it to electron beam radiation of 1 to 20 megarads or corona discharge.

DETAILED DESCRIPTION OF THE INVENTION

In amplification of the above summary, the process of the invention is carried out by:

(1) contacting, for at least one second, a surface of a solid shaped structure with a solution containing:

(a) at least 0.1 wt. % of a crosslinkable hydrophilic polymer; and optionally containing

(b) (i) a thermally-activated free radical initiator; or

(ii) an ultraviolet light-activated free radical initiator;

(2) drying, for example, air drying, the coated surface; and

(3) crosslinking the hydrophilic polymer of the dried coated surface, as further described below.

If a thermally-activated free radical initiator is used in the coating solution, the coated surface is heated to the decomposition temperature of the free radical initiator, to effect crosslinking of the hydrophilic polymer. The length of time that the coated surface is exposed to the elevated temperature is determined by the half-life of the initiator. The exposure time should be of a duration as to consume substantially all of the initiator.

If an ultraviolet light-activated free radical initiator, such as benzoin or benzoin methyl ether, is used in the coating solution, the coated surface is subjected to ultraviolet radiation to effect crosshydrophilic polymer. The length of time that the coated surface is exposed to the UV light is determined by the intensity of the light source and the half-life of the initiator. The exposure time should be of a duration to consume substantially all of the initiator.

The process of this invention can be carried out using a combination of thermal and UV-activated initiators.

The ratio of the number of moles of initiator (thermal or UV-activated) per gram of uncrosslinked hydrophilic polymer used in the process usually is in the range 0.0002 to less than 0.0040, although it has been discovered that with some substrates higher ratios can be tolerated, for example, substrates comprised of Estane™ or Lycra™, both of which substrates are exemplified herein. Stated more generally, an effective amount of initiator is employed, "effective amount" being that amount which provides the requisite crosslinking of crosslinkable

hydrophilic polymer so as to achieve a durable coating that exhibits a low coefficient of friction when wet.

Alternatively, the process can be carried out by contacting the solid surface with a solution consisting of uncrosslinked hydrophilic polymer, air drying the coated surface, and subjecting it to electron beam radiation of 1 to 20 megarads or corona discharge for a period of 0.03 to 5 minutes, to effect crosslinking of the polymer.

The crosslinking of hydrophilic polymer can be effected in air or in an inert atmosphere, such as nitrogen, helium, argon or carbon dioxide. The degree of crosslinking is important and is controlled by the operating conditions chosen. Too much crosslinking reduces or completely eliminates the low friction surface property, and too little crosslinking negatively affects the durability of the coating. In addition, it is to be noted that the crosslinking must be carried out on relatively dry hydrophilic polymer. It has been discovered that hydrophilic polymer crosslinked in the presence of water may produce an adhesive surface, rather than a surface having a low coefficient of friction.

Examples of crosslinkable hydrophilic polymers that can be used herein include, but are not intended to be limited to, poly(N-vinylpyrrolidones), such as poly(N-vinyl-2-pyrrolidone), a preferred polymer herein, and poly(N-vinyl-3-pyrrolidone); substituted poly(N-vinyl-2-and-3-pyrrolidones) in which one or more of the hydrogen atoms of the ring are substituted with one or more substituents selected from -CH₃, -C₂H₅, -OCH₃ and -OC₂H₅; poly(N-vinyl-2-piperidone); poly(N-

vinyl-3-piperidone); poly(N-vinyl-4-piperidone); substituted poly(N-vinyl-2-, 3- and 4-piperidones) in which one or more of the hydrogen atoms of the ring are substituted with one or more substituents selected from -CH₃, -C₂H₅ -OCH₃ and -OC₂H₅;

5 poly(methylvinyl ether); polyacrylic acid; polymethacrylic acid; polyethylene oxide; partially esterified polymethacrylic acid; polymethacryl amide; partially esterified polyacrylic acid;

10 polyacrylamide; methyl cellulose; poly(2 hydroxyethyl methacrylate); and mixtures of the above.

15 The crosslinkable hydrophilic polymers of this invention may be blended with nonhydrophilic polymers prior to coating the solid substrate, for example in the coating solution. The proportions of hydrophilic and nonhydrophilic polymer should be such that a hydrophilic surface is ultimately formed on the solid substrate and would be readily apparent to one skilled in the art. It is preferred that the hydrophilic polymer be the major portion of the blend. A useful nonhydrophilic polymer is polyurethane.

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25 Examples of thermally-activated free radical initiators that can be used herein include, but are not intended to be limited to, peroxide initiators, such as benzoyl peroxide, peracetic acid, perbenzoic acid, hydrogen peroxide, t-butylhydroperoxide, bis(4-t-butylidicarbonate, t-butylperoxypivalate, t-butylperoctoate, diisopropylbenzene hydroperoxide, succinic acid peroxide, potassium persulfate and ammonium persulfate. Although not wishing to be bound by this explanation, it is believed that any thermally-activated free radical initiator that

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produces a stabilized free radical, such as one containing a -CN or -COOR ester group adjacent to the radical site, does not have sufficient energy to effect crosslinking of the hydrophilic polymer.

5 Solvents which are suitable for dissolving the hydrophilic polymer include, but are not intended to be limited to, water, methylene chloride, chloroform, low molecular weight alcohols, such as methanol or ethanol, dimethylformamide (DMF), dimethylacetamide, ethyl acetate, methylethylketone, ethylene dichloride, acetone, esters of lactic acid, for example, ethyl lactate, diacetone alcohol, N-methylpyrrolidone, pyridine and the mono- and diethylene glycol ethers.

10 15 The concentration of uncrosslinked hydrophilic polymer in the solution is not critical. It will readily be understood that the use of higher concentrations can be used to produce thicker coatings of crosslinked hydrophilic polymer.

20 Likewise, the molecular weight of the uncrosslinked hydrophilic polymer is not critical, although it is preferred to utilize uncrosslinked hydrophilic polymer having a molecular weight of at least 1,000, more preferably at least 10,000.

25 30 Although the above description recites that the hydrophilic polymer is in solution, it is not essential that such be the case. More specifically, the uncrosslinked hydrophilic polymer can be applied to the solid surface by any feasible means. For example, the uncrosslinked hydrophilic polymer can be in the form of a dispersion, or it can be spray-coated onto the surface, etc., all as will be apparent to one skilled in the art.

It is to be understood that the invention

herein resides only in those coated substrate
structures, and processes for producing such
structures, wherein the crosslinked coatings have a
low coefficient of friction when wet and are durably
5 adhered to the substrate. Although not wishing to
be bound by this explanation, the adherence of the
hydrophilic crosslinked polymer to the surface of
the substrate is believed to be by physical forces
rather than by chemical bonding, as evidenced by the
10 fact that crosslinked hydrophilic polymer adheres
strongly to metal surfaces, such as steel and
aluminum, provided the aforesaid initiator to
polymer ratio is correctly chosen. The durability
of the crosslinked hydrophilic polymer on the
15 surface of the coated article is determined by
soaking the article in water at 37°C and
periodically testing the surface when wet for the
coefficient of friction. If the coefficient of
friction is unaffected after one hour, the coating
20 is considered durable. The time of one hour has
been arbitrarily chosen, since most non-durable
coatings of the art, regardless of their type, will
fail in less than one hour.

25 The low coefficient of friction, when wet, of
the coated surface can be determined qualitatively
by rubbing one's fingers on the wetted sample and
comparing it to the feel of an uncoated wet
substrate. The kinetic coefficient of friction can
be determined quantitatively by using a standard
30 test, such as ASTM D1890-61T or ASTM D1894-78.
Values of the coefficient of friction determined by
these tests show quantitative differences in the dry
and wet state of coated materials being tested.
Mixtures of uncrosslinked hydrophilic polymer and

other compatible polymers can be employed in carrying out the process of the invention. The amount of the compatible polymer which can be admixed with the uncrosslinked hydrophilic polymer can readily be determined experimentally, with the upper limit being just below that which substantially deleteriously affects the benefits achieved by the invention, that is, the production of a durable coated solid surface having a low coefficient of friction when wet.

The solid substrates whose surfaces can be coated in accordance with this invention can be organic or inorganic and include polymers, metals, wood, natural fibers and synthetic fibers. More specifically, these substrates include polymers, such as polyurethanes, for example, Estane™, polyesters, for example, Mylar™ or Rynite™, fluoropolymers such as "Tefzel" Modified ETFE fluorocarbon and "Viton" fluoroelastomer, perfluoropolymers such as "Kalrez" perfluoroelastomer and "Teflon" fluorocarbon resin, polyacetals such as "Delrin" acetal resins, polyamides, polyimides, polyolefins, polyvinyl halides, polycarbonates, cellulosics, cured epoxy resins, natural and synthetic rubbers, and silicones; metals, such as steel, stainless steel, aluminum, iron and copper; natural fibers such as cotton and wool; and synthetic fibers, such as Dacron™ polyester fiber. Preferred fluoropolymers and perfluoropolymers are homo- or copolymers of tetrafluoroethylene. Other preferred fluoropolymers include homo- and copolymers of vinylidene fluoride. Non-polar surfaces, such as polyolefins, should be made polar prior to the coating operation by

pretreatment, for example, with corona discharge, flame treatment, or chemical etching with permanganate or chromium trioxide.

5 If the solid substrate is a polymer, such polymers shall include, but not be limited to, crystalline, semicrystalline, glassy amorphous and elastomeric polymers. Polymers may contain additives such as filler, pigments, antioxidants, antiozonants, etc.

10 Solid substrates shall also include any surface that is covered with a coating, such as paint. In this case, surface preparation, if needed, would be to the coating surface, not the substrate underneath.

15 It has been discovered that if a surface is difficult to coat and render slippery, the advantageous effects of the invention can be realized by first coating the surface with a material which is known to provide the desirable results of the invention. For example, it has been found that Pellethane™, a polyurethane which, for some unknown reason, is difficult to render slippery in accordance with this invention, can be coated with Estane™ and then subjected to the process of

20 25 the invention.

30 The process of this invention provides a solid substrate surface with a durable hydrophilic coating having a low coefficient of friction in wet condition. In addition, some of the coatings of the invention have been found to exhibit the properties of biocompatibility, blood compatibility, non-fouling and anti-fogging, with minimal change in profile (width, thickness, etc.) in either the wet or dry condition. Such coatings may be suitable for

medical applications, for example, catheters; scopes, such as endo and laryngo; tubes, such as feeding, draining and endotracheal; wound dressings; contact lenses; eye shields having improved 5 cleanability; implants; condoms; extracorporeal blood conduits; hemodialysis membranes; blood filters; and circulatory assist devices. Other applications may include food packaging; boat hulls; razor blades; fishing nets; conduits for wiring; low friction coatings on torpedoes; internally coated pipes and tubes for moving large volumes of fluids; membranes for separations; glassware; 10 sporting/recreational equipment; cosmetic additives (spreading agent); mold release agents; fishing lines and regenerable cookware coatings.

15 The invention is illustrated in the following examples. In the examples and comparative experiments, PVP refers to poly(N-vinyl-2-pyrrolidone), a preferred hydrophilic polymer, as noted above.

EXAMPLE 1

20 A polyurethane film [Texin™ 480 AR] was placed into a Petri dish and contacted with a solution containing 0.5 g of benzoyl peroxide, 48 g of methylene chloride and 1.5 g of PVP [MW 360,000] for 10 minutes. The film was air dried for 10 minutes at 25°C, placed in a one quart jar and purged with nitrogen for three h. The jar was 25 sealed and heated at 90°C for one h.

30 The film exhibited low friction in water at 37°C. The low friction in water at 37°C persisted undiminished for at least three days.

EXAMPLE 2

A polyurethane film [Texin™ 480 AR] was dipped into a 3% solution of PVP [MW 360,000] in methylene chloride for 30 minutes. The film was drained and air dried for several h. It was then placed in a Petri dish contained in a glove bag under an atmosphere of argon. The film was then treated with 10 megarads of electron beam radiation.

The film exhibited low friction in water at 37°C. The low friction in water at 37°C persisted undiminished for at least six days.

EXAMPLE 3Crosslinked PVP Films on Metals and Plastics

The coating solution consisted of 3 g of PVP [MW 360,000], 1 g of benzoyl peroxide, and 96 g of methylene chloride. The materials being tested were dipped one-half of their length into the solution and removed. The excess solvent was allowed to drain off. After air drying, the films were cured by heating at 110°C for one hour in air. The materials coated were:

1. Steel panel [type used for paint testing]
2. Mylar™ [polyethylene terephthalate film]
3. Aluminum foil [1 mil (0.0254 mm) thick]

All exhibited a low coefficient of friction in water. The coatings remained slippery after four days in water at 23°C. The steel panel rusted extensively in the uncoated areas, but not under the crosslinked PVP. After four days, the aluminum foil was dried and the coating thickness was found to be about 0.1 mil (0.00254 mm). The Mylar™ film was rinsed, dried, placed in a polyethylene bag, and cooled to 0°C. The film was quickly removed from the

bag and breathed upon. The coated area remained clear whereas the uncoated area became fogged.

This example shows that the invention is useful with metals and plastics, where there is no polymer penetration of the solid surface.

Therefore, there need be no concern with polymer supports about grafting of the two polymers.

EXAMPLE 4

Dependence on the Molecular Weight of the Uncrosslinked Polymer

There seems to be no dependence on molecular weight as illustrated by the following experiments.

Solutions consisting of 3 g of PVP, 96 g of methylene chloride, and 1 g of benzoyl peroxide were coated onto 1 mil (0.0254 mm) aluminum foil. After drying and curing at 110°C for one hour, they were soaked in water at 23°C.

1. PVP molecular weight 10,000
2. PVP molecular weight 24,000
3. PVP molecular weight 40,000
4. PVP molecular weight 160,000

All films were slippery in water, that is, exhibited a low coefficient of friction.

EXAMPLE 5

Coefficient of Friction Data

A film of Estane™ commercially available polyurethane was hot pressed onto a steel panel measuring 4" x 12" (10.2 x 30.5 cm). The polyurethane surface was coated by dipping for 20 seconds in a solution consisting of 1 g of benzoyl peroxide, 3 g of PVP [MW 360,000] and 96 g of methylene chloride. After drying under nitrogen

overnight, the panel was heated one hour in air at 110°C, then washed in water at 37°C for one hour.

The coated surface was rubbed with soft paper towed to remove any debris and tested for 5 coefficient of friction [ASTM D1894-78] against polyurethane as the second surface.

The experiment was repeated, using polytetrafluoroethylene and polyvinyl chloride instead of the steel.

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Kinetic Coefficient of Friction of Untreated Estane™

Dry	Wet
2.35	0.59

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Kinetic Coefficient of Friction of Crosslinked PVP-Coated Estane™

Dry	Wet
0.30	0.09

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Kinetic Coefficient of Friction of Untreated Estane™ on polytetrafluoroethylene (PTFE)

Dry	Wet
0.27	0.17

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Kinetic Coefficient of Friction of Crosslinked PVP-Coated Estane™ on PTFE

Dry	Wet
0.20	0.10

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Kinetic Coefficient of Friction of Untreated Estane™ on polyvinyl chloride (PVC)

Dry	Wet
0.55	0.39

Kinetic Coefficient of Friction of Crosslinked PVP-
Coated Estane™ on PVC

Dry Wet

0.22 0.10

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EXAMPLE 6

PVP Crosslinked With t-Butyl Peroctoate

The coating solution consisted of 3 g of PVP (MW 360,000), 2 g of t-butylperoctoate, and 95 g of methylene chloride. A stainless steel sheet and Mylar™ 500D polyester film were coated with the solution using a 10 mil (0.254 mm) doctor knife. After air drying, the coatings were cured at 100-110°C for one hour. Their slippery nature persisted undiminished for at least seven days in water at 37°C.

EXAMPLE 7

Crosslinked Coatings Of Polyvinylpyrrolidone (PVP)

On Lycra™ Film

A. Lycra™ films were coated with the following PVP [MW 360,000] solutions using a 10 mil (0.254 mm) doctor knife:

1) 3 g of PVP, 1 g of benzoyl peroxide, 96 g of methylene chloride

2) 3 g of PVP, 2 g of benzoyl peroxide, 95 g of methylene chloride

3) 3 g of PVP, 3 g of benzoyl peroxide, 94 g of methylene chloride.

After the solvent had evaporated, the coated Lycra™ was cured at 110°C for one hour. All three films were slippery in water for at least one day.

B. A balloon made of the same Lycra™ was

similarly treated with Solution 1 and another with Solution 1 diluted with an equal volume of methylene chloride. Both balloons were very slippery in water.

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EXAMPLE 8Effect of Using Too Much Peroxide

A. Solutions containing 3% PVP in methylene chloride with: 1) 1% benzoyl peroxide, and 2) 3% benzoyl peroxide were coated onto MylarTM 500D film, air dried, and cured at 110°C for 1 hour. Solution 1 gave a slippery film in water, but Solution 2 did not give a slippery surface in water.

B. Solution 2 did not give a slippery film in water on aluminum foil or stainless steel.

Too much crosslinking gives a non-slippery surface.

EXAMPLE 9

Catheter tubes made of polyurethane filled with 30 wt. % BaSO₄, 1 wt. % titanium dioxide and 0.5 wt. % green pigment were coated by dipping for 20 seconds into a solution consisting of 1 g of benzoyl peroxide, 3 g of PVP [MW 360,000] and 96 g of methylene chloride. After drying under nitrogen overnight, the tubes were heated one hour in air at 110°C, then washed in water at 37°C for one hour. The coated tubes were tested for coefficient of friction using the ASTM D1890-61T procedure against plasticized polyvinyl chloride as the second surface. The results are shown below.

Kinetic Coefficient of Friction

	Dry	Wet
[Average of 5 samples]	0.22	0.03

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EXAMPLE 10

The coating solutions consisted of 3 g of poly-acrylic acid [solution 1: MW 90,000; solution 2: MW 250,000], 0.5 g of succinic acid peroxide, and 96.5 g of water. Mylar™, Estane™ and aluminum foil were coated with the above solutions. The excess solvent was allowed to drain off. After air drying, the films were cured by heating at 100°C for one hour in air. The surface of the coated materials when in contact with water exhibited a low coefficient of friction for at least seven days at room temperature. A repeat of the above experiment using 1, 2, and 3 wt. % of succinic acid peroxide in the coating solution gave similar results.

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EXAMPLE 11

The coating solution consisted of 3 g of methyl cellulose, 0.5 g of succinic acid peroxide, and 96 g of water. Estane™ and aluminum foil were coated with the above solution. The excess solvent was allowed to drain off. After air drying, the films were cured by heating at 100°C for one hour in air. The surface of the coated materials when in contact with water exhibited a low coefficient of friction for at least two hours. A repeat of the above experiment using 1 g, 2 g, and 3 g of succinic acid peroxide in the coating solution gave similar results.

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EXAMPLE 12

5 The coating solution consisted of 3 g of poly-(methylvinyl ether), 0.5 g of benzoyl peroxide, and 96.5 g of toluene. Estane™ and aluminum foil were coated with the above solution. The excess solvent was allowed to drain off. After air drying, the films were cured by heating at 100°C for one hour in air. The surface of the coated materials when in contact with water exhibited a low coefficient of friction. A repeat of the above experiment using 1, 2, and 3 wt. % of benzoyl peroxide in the coating solution gave similar results.

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EXAMPLE 13

20 A panel of smooth, gel coated, polyester/glass boat hull was coated with a solution consisting of 3 wt. % of PVP [MW 360,000] and 2 wt. % of benzoyl peroxide in methylene chloride by dipping the panel for 30 seconds. The excess solution was drained off by placing the panel vertically in a large beaker saturated with methylene chloride vapors. The vapors were allowed to escape slowly until the coating was dry; it was then cured at 100°C for 20 minutes. The high points on the finish were removed by light sanding with extremely fine sandpaper of the coated panel when in contact with water exhibited a low coefficient of friction.

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EXAMPLE 14

A Mylar™ film coated with crosslinked PVP

was tested for coefficient of friction using methanol and ethanol as the wetting agents. The film when in contact with ethanol or methanol exhibited a low coefficient of friction.

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EXAMPLE 15

A solution containing 3% PVP (molecular weight 360,000) and 2% of benzoyl peroxide in methylene chloride was prepared. Two samples of silicone tubing, one untreated and other plasma treated, were dipped into the above solution for 30 sec. The tubes were purged with nitrogen and then allowed to air dry for 3 days. The coating was then crosslinked by heating at 110 deg. for 70 min. After two hours in a 38 deg. agitated water bath, both silicone tubing samples were slippery when wet.

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EXAMPLE 16

Using the same procedure as Example 15, strips of "Delrin" 100ST acetal resin (available from E. I. du Pont de Nemours) were dipped into the PVP solution. After air drying, the strips were heated 110 deg. for 70 min. After 2 hr. in a 38 deg. agitated water bath the surfaces were still slippery.

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EXAMPLE 17

Using the same procedure as Example 15 pieces of Hytrel 4056 polyester elastomer (available from E. I. du Pont de Nemours) were dipped in the PVP solution for 5 sec. After air drying overnight they were heated at 110 deg. for 70 min. After 2 hr. in an agitated water bath at 38 deg., they were very slippery.

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EXAMPLE 18

Using the procedure of Example 15, pieces of "Kalrez" perfluoroelastomer (available from E. I. du Pont de Nemours) were treated with the PVP solution for 5 min. After air drying overnight the pieces were heated at 100 deg. for 70 min. After immersion in a 38 deg. agitated water bath for 2 hr., the pieces were slippery.

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EXAMPLE 19

Using the same procedure as Example 15, pieces of "Rynite" 530-NC-10 polyester engineering thermoplastic were immersed in the PVP solution for about 4 min. "Rynite" 530-NC-10 (available from E. I. du Pont de Nemours) is poly(ethylene terephthalate) containing 30% by weight glass fiber. After air drying 3 days, the pieces were heated at 100 deg. for 70 min. The resulting pieces were very slippery after wetting with distilled water.

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COMPARATIVE EXPERIMENT 1

PVP [20% aqueous solution] was poured into Petri dishes, placed in polyethylene bags, and purged with nitrogen. The sealed bags were passed under an electron beam. After 1 megarad exposure, the viscosity increased; after 2 megarad exposure, the solution was a gel. The gels receiving 2, 5, 10 or 20 megarads were strongly adhesive; even wet fingers stick strongly to them. This is in contrast to films that have been crosslinked in a dry state which are very slippery when wet. A catheter coated with PVP crosslinked in the presence of water would be so adhesive it could not be inserted into the body.

COMPARATIVE EXPERIMENT 2

5 In this experiment, the PVP was admixed with a polyurethane to facilitate swelling of the coating, so as to provide intimate contact between the coating and the water in which it is subsequently soaked.

10 The following two solutions were combined:

1. 2 g of PVP [MW 360,000] in 13 mL of DMF
2. 2 g of Texin™ 480 [polyurethane] in 13 mL of DMF

15 The final solution had increased viscosity but no phase separation. A film was prepared by casting the solution at 145°C. There was no phase separation. The film had a 99.6% weight gain after soaking 7 hours in water at 25°C, and a 118% weight gain after 72 hours.

20 When dried, the film had lost 3% of its weight due to the PVP that had been extracted.

25 The results of this experiment show that the amount of swelling which will be realized may have to be taken into consideration when selecting the hydrophilic polymer for certain applications.

COMPARATIVE EXPERIMENT 3

30 The following experiment shows the importance of crosslinking the PVP, and the absence of durability in a coating which is comprised of uncrosslinked PVP.

Polyurethane film was coated with a 3 wt. % solution of PVP [MW 360,000] in methylene chloride. The film was dried at 25°C for 24 hours, then at 100°C for one hour.

The surface of the coated material when in

contact with water exhibited a low coefficient of friction. However, when the film was immersed in water at 37°C, the low coefficient of friction was lost in about one hour, demonstrating the non-durability of non-crosslinked polymer.

CLAIMS

5 1. Solid shaped structure having a surface coated with crosslinked hydrophilic polymer, the coating being durable and exhibiting a low coefficient of friction when wet.

10 2. Solid shaped structure of Claim 1 wherein the crosslinked polymer is selected from poly(N-vinyl-3-pyrrolidone); substituted poly-(N-vinyl-2- and 3-pyrrolidones) in which one or more of the hydrogen atoms of the ring are substituted with one or more substituents selected from -CH₃, -C₂H₅, -OCH₃ and -OC₂H₅; poly(N-vinyl-2-piperidone); poly(N-vinyl-3-piperidone); poly(N-vinyl-4-piperidone); substituted poly(N-vinyl-2-, 3- and 4-piperidones) in which one or more of the hydrogen atoms of the ring are substituted with one or more substituents selected from -CH₃, -C₂H₅,

15 -OCH₃ and -OC₂H₅; poly(methylvinyl ether); polyacrylic acid; polymethacrylic acid; polyethylene oxide; partially esterified polymethacrylic acid; polymeth-acrylamide; partially esterified polyacrylic acid; polyacrylamide; methyl cellulose; poly(2-hydroxyethyl methacrylate); and mixtures thereof.

20 3. The structure of Claim 1 wherein the crosslinked hydrophilic polymer is blended with a nonhydrophilic polymer prior to coating.

25 4. Shaped structure of Claim 1 wherein the polymer is poly(N-vinyl-2-pyrrolidone).

30 5. Shaped structure of Claim 1 in the form of a tube.

6. Shaped structure of Claim 1 in the form of a fiber.

7. Shaped structure of Claim 1 in the form of a containment vessel.

8. Shaped structure of Claim 1 in the form of a film.

5 9. Shaped structure of Claim 1 comprising an, organic substrate coated with crosslinked hydrophilic polymer.

10 10. Shaped structure of Claim 1 comprising an inorganic substrate coated with crosslinked hydrophilic polymer.

11. Shaped structure of Claim 9 wherein the organic substrate is polymeric.

12. Shaped structure of Claim 9 wherein the organic substrate is a polyurethane.

15 13. Shaped structure of Claim 10 wherein the inorganic substrate is a metal.

14. Shaped structure of Claim 13 wherein the metal is aluminum.

20 15. Shaped structure of Claim 13 wherein the method is stainless steel.

16. The structure of Claim 3 wherein the hydrophilic polymer is the major portion of the blend.

25 17. The structure of Claim 16 wherein the nonhydrophilic polymer is polyurethane.

18. Shaped structure of Claim 9 wherein the organic substrate is a perfluoropolymer.

19. Shaped substrate of Claim 9 wherein the organic substrate is a fluoropolymer.

30 20. Shaped structure of Claim 9 wherein the organic substrate is a polyacetal.

21. Process comprising contacting and adherably coating a surface of a solid shaped structure with a crosslinkable hydrophilic polymer,

drying the resulting coated surface, if necessary, and crosslinking the polymer.

22. Process of Claim 21 wherein the crosslinkable hydrophilic polymer is selected from poly(N-vinyl-2-pyrrolidone); poly(N-vinyl-3-pyrrolidone); substituted poly(N-vinyl-2- and 3-pyrrolidones) in which one or more of the hydrogen atoms of the ring are substituted with one or more substituents selected from -CH₃, -C₂H₅, -OCH₃ and -OC₂H₅; poly(N-vinyl-2-piperidone); poly(N-vinyl-3-piperidone); poly(N-vinyl-4-piperidone); substituted poly(N-vinyl-2-, 3- and 4-piperidones) in which one or more of the hydrogen atoms of the ring are substituted with one or more substituents selected from -CH₃, -C₂H₅; poly(methylvinyl ether); polyacrylic acid; polymethacrylic acid; polyethylene oxide; partially esterified polymethacrylic acid; polymethacrylamide; partially esterified polyacrylic acid; polyacrylamide; methylcellulose; poly(2-hydroxyethyl methacrylate); and mixtures thereof.

23. Process of Claim 21 wherein the crosslinkable hydrophilic polymer is in solution, and the resulting coated surface is dried to remove the solution solvent.

24. Process of Claim 21 wherein the crosslinking is effected by means of electron beam radiation of 1 to 20 megarads or corona discharge.

25. Process of Claim 24 wherein the crosslinking is effected in an inert atmosphere.

30 26. Process of Claim 25 wherein the inert atmosphere is selected from nitrogen, argon, helium and carbon dioxide.

27. Process of Claim 24 wherein the crosslinking is effected in air.

28. Process of Claim 23 wherein the solution of crosslinkable hydrophilic polymer includes an effective amount of a free radical initiator selected from thermally-activated and ultraviolet light-activated free radical initiators.

5 29. Process of Claim 28 wherein the ratio of the number of moles of initiator per gram of polymer is within the range 0.0002 to less than 0.0040.

10 30. Process of Claim 28 wherein the thermallyradical initiator is a peroxide.

15 31. Process of Claim 28 wherein the initiator is a thermally-activated free radical initiator and crosslinking is effected in an inert atmosphere by heating to decompose the free radical initiator.

32. Process of Claim 31 wherein the inert atmosphere is selected from nitrogen, argon, helium and carbon dioxide.

20 33. Process of Claim 28 wherein the crosslinking is effected in air.

25 34. Process of Claim 31 wherein the free radical initiator is selected from benzoyl peroxide, peracetic acid, perbenzoic acid, hydrogen peroxide, t-butylhydroperoxide, bis(4-t-butylcyclohexyl)peroxy-dicarbonate, t-butylperoxypivalate, t-butylperooctoate, diisopropylbenzene hydroperoxide, succinic acid peroxide, potassium persulfate and ammonium persulfate.

30 35. Process of Claim 33 wherein the free radical initiator is selected from benzoyl peroxide, peracetic acid, perbenzoic acid, hydrogen peroxide, t-butylhydroperoxide, bis(4-t-butylcyclohexyl)peroxy-dicarbonate, t-butylperoxypivalate, t-butylperooctoate,

diisopropylbenzene hydroperoxide, succinic acid peroxide, potassium persulfate and ammonium persulfate.

36. Process of Claim 28 wherein the free radical initiator is an ultraviolet light-activated initiator and crosslinking is effected by means of ultraviolet radiation which activates the free radical initiator.

37. Process of Claim 36 wherein the crosslinking is effected in an inert atmosphere.

38. Process of Claim 37 wherein the inert atmosphere is selected from nitrogen, argon, helium and carbon dioxide.

39. Process of Claim 36 wherein the crosslinking is effected in air.

40. Process of Claim 36 wherein the free radical initiator is benzoin or benzoin methyl ether.

41. Process of Claim 21 further comprising:

(1) contacting, for at least one second, a surface of a solid shaped structure with a solution containing:

(a) at least 0.1 wt. % of a crosslinkable hydrophilic polymer; and

(b) (i) a thermally-activated free radical initiator; or

(ii) an ultraviolet light-activated free radical initiator;

(2) drying the coated surface; and

(3) crosslinking the hydrophilic polymer of the dried coated surface.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 89/00720

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC ⁴ C 09 D 3/00; C 09 D 5/00; C 08 J 7/04; B 05 D 3/00;
C 08 L 39/06

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁴	C 09 D; C 08 J; B 05 D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT*

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP, A, 0093094 (ASTRA MEDITEC AB) 2 November 1983 see claims 1-10; page 2, line 15 - page 6, line 2	1,2,3,5,9, 11,12,16,17, 21,22,23
Y	--	1-6,8-17, 21-23,28, 36,41
X	DE, A, 2608827 (KONISHIROKU PHOTO INDUSTRY CO. LTD) 23 September 1976 see claims; page 7, line 1 - page 8, line 1; page 11; line 19 - page 12, line 1	21-23,28-30, 36,39
Y	US, A, 3892575 (R.E. WATTS et al.) 1 July 1975 see claims 1-4; column 1, line 30 - column 2, line 56; column 3, line 44 - column 5, line 2; column 6, lines 14-26; example 7 --	1-6,8-17, 21-23,28, 36,41 --
		./.

* Special categories of cited documents: ¹⁰"A" document defining the general state of the art which is not
considered to be of particular relevance"E" earlier document but published on or after the international
filing date"L" document which may throw doubts on priority claim(s) or
which is cited to establish the publication date of another
citation or other special reason (as specified)"O" document referring to an oral disclosure, use, exhibition or
other means"P" document published prior to the international filing date but
later than the priority date claimed"T" later document published after the international filing date
or priority date and not in conflict with the application but
cited to understand the principle or theory underlying the
invention"X" document of particular relevance; the claimed invention
cannot be considered novel or cannot be considered to
involve an inventive step"Y" document of particular relevance; the claimed invention
cannot be considered to involve an inventive step when the
document is combined with one or more other such documents,
such combination being obvious to a person skilled
in the art.

"Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

8th June 1989

Date of Mailing of this International Search Report

8 JUN 1989

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

R.C.G. VAN DER PUTTEN

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4589873 (A. SCHWARTZ et al.) 20 May 1986 see claims	1-5,8,9, 11,12,18, 19,21,22, 23

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8900720
SA 27375

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 23/06/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A- 0093094	02-11-83	SE-B-	430696	05-12-83
		AU-B-	556350	30-10-86
		AU-A-	1326683	27-10-83
		CA-A-	1215598	23-12-86
		GB-A, B	2119283	16-11-83
		JP-A-	58193766	11-11-83
		SE-A-	8202524	23-10-83
		US-A-	4459317	10-07-84
		US-A-	4487808	11-12-84
DE-A- 2608827	23-09-76	JP-A-	51101077	07-09-76
		GB-A-	1549317	01-08-79
		US-A-	4051302	27-09-77
US-A- 3892575	01-07-75	GB-A-	1420064	07-01-76
US-A- 4589873	20-05-86	None		